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Nucleophilic Substitution at Bivalent Sulphur: the Alkaline Hydrolysis of Esters of Arylsulphenic Acids

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NUCLEOPHILIC substitution reactions at bivalent sulphur have received relatively little attention and almost all the kinetic work in this field has dealt with reactions of type (1) in which an S–S bond has been broken.[1] A recent report of a kinetic study of the hydrolysis of arylsulphenyl chlorides,[2] ArSCl, a reaction of type (2) in which the bond being broken involves an atom other than sulphur prompts us to present a preliminary account of a similar reaction, the alkaline hydrolysis of alkyl esters of arylsulphenic acids, ArSOR.

$$\mathrm{N^- + R{-}S{-}S{-}Y \rightarrow N{-}S{-}R + YS^-} \qquad (1)$$

$$\mathrm{N^- + R{-}S{-}Y \rightarrow N{-}S{-}R + Y^-} \qquad (2)$$

The hydrolysis of alkyl 4-substituted-2-nitrobenzenesulphenates in aqueous ethanol solution using an excess of sodium hydroxide was shown to give the corresponding disulphide in approximately 66% yield, together with the salt of the corresponding sulphinic acid. By analogy with known reactions[3] and in accordance with the product isolations, the following reaction scheme may be postulated:

$$\mathrm{ArSOR + OH^- \rightarrow ArSOH + OR^-}$$

$$\mathrm{ArSOH + OH^- \rightleftharpoons ArSO^- + H_2O}$$

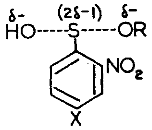
$$\mathrm{2ArSOH \rightarrow ArSO{\cdot}SAr + H_2O}$$

$$\mathrm{2ArSO{\cdot}SAr \rightarrow ArSO_2{\cdot}SAr + ArS{\cdot}SAr}$$

$$\mathrm{ArSO_2{\cdot}SAr + OH^- \rightarrow ArSO_2^- + ArSOH}$$

The rate of disappearance of ester at 25° in 50% *v/v* aqueous ethanol in the presence of excess of hydroxide ion was measured spectrophotometrically using the band at approximately 400 mμ. The graph of the first-order velocity constants so obtained against the concentration of hydroxide ion showed a slight curvature, and passed through or near the origin indicating that the uncatalysed reaction is very slow. The logarithms of the derived second-order velocity constants decreased linearly with increasing ionic strength, and by extrapolation the second-order velocity constant at zero ionic strength was obtained. The results are given in the Table. During the reaction, bands at approximately 350 and 580 mμ attributable[4] to the sulphenate anion, $\mathrm{ArSO^-}$, were observed. These bands simultaneously reached a maximum and then decayed to zero optical density. The relationship between the maximum optical density of these bands and the concentration of the reagents is in agreement with the above reaction scheme.

From a consideration of the relative rates of hydrolysis for the alkyl 2-nitrobenzenesulphenates and from the similarity of the products obtained in this reaction to those obtained from the alkaline hydrolysis of other arylsulphenyl derivatives,[3a] we consider that the reaction involves a nucleophilic attack by hydroxide ion at the sulphur atom. Unlike the hydrolysis of arylsulphenyl chlorides in chloroform containing water,[2] the values of log k_2^0 for the alkaline hydrolysis of the ethyl 4-substituted-2-nitrobenzenesulphenates in aqueous ethanol solution do not give a linear Hammett plot, but both electron-releasing and electron-withdrawing substituents increase the rate of reaction relative to that of the unsubstituted compound. This type of behaviour, which is similar to that observed[5a] for the reaction of substituted benzyl bromides with nucleophiles, is interpreted as indicating different degrees of bond formation and fission in the transition state.[5] These data therefore support the transition state:



which is similar to that suggested by Fava[6] for the exchange reactions of disulphides and alkylthiosulphates, rather than one which involves participation by a *d*-orbital on the sulphur.[7]

TABLE *Second-order velocity constants at zero ionic strength for the alkaline hydrolysis of* $\mathrm{4\text{-}X\text{-}2\text{-}NO_2{\cdot}C_6H_3{\cdot}SOR}$ *in* 50% v/v *aqueous ethanol at* 25°.

X	H	H	H	H	MeO	Me	Cl	$\mathrm{CF_3}$
R	Me	Et	$\mathrm{Pr^i}$	$\mathrm{Bu^t}$	Et	Et	Et	Et
$10^3k_2^{\circ}$(l.mole sec.$^{-1}$)	5·8	4·7	3·3	0·52	17·2	5·7	14·0	6·9

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The importance of steric effects in this reaction is shown by the linearity of the graph of log k_2^0 for the alkyl 2-nitrobenzenesulphenates against the alkyl steric parameter, E_S,[8] the value for δ being 0·6. Further work is in progress to test the validity of this correlation.

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